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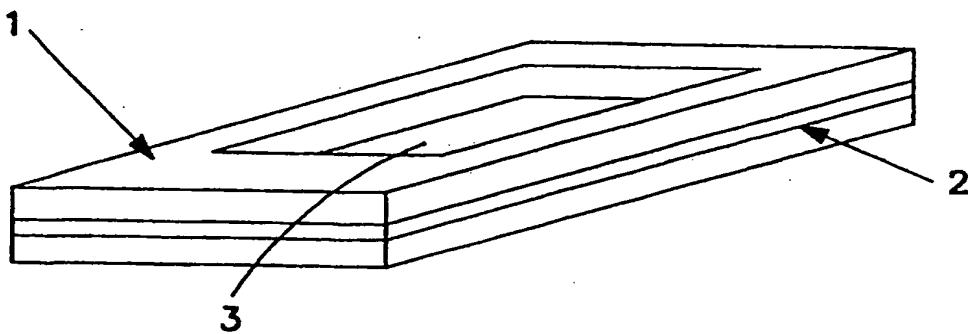
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(54) Title: A MEMBRANE ELECTRODE GASKET ASSEMBLY



(57) Abstract

An improved membrane electrode assembly (MEA) sealant having a gasket and a sub-gasket to seal the MEA and to protect it from possible edge failures. The gasket is typically a support structure such as porous expanded PTFE impregnated with an ionomer. The sub-gasket comprises a thermoplastic polymer such as polytetrafluoroethylene or expanded PTFE. The sub-gasket is disposed over a peripheral portion of the polymer electrolyte membrane such that said sub-gasket also extends over the portion of the electrode extending over the peripheral portion of the polymer electrolyte membrane.

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A MEMBRANE ELECTRODE GASKET ASSEMBLY

FIELD OF INVENTION

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This invention relates to membrane electrode assemblies that are useful in electronic devices such as fuel cells. More particularly, this invention relates to sealing elements (also referred to as "gaskets") useful in connection with such membrane electrode assemblies.

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BACKGROUND

Ion-exchange membranes, also known as polymer electrolyte membranes (PEMs), are frequently used in fuel cells and other electrochemical devices such as chloralkali cells or electrodialysis cells. In all of these 15 applications, the ion-exchange membrane is located in a container between two electrodes (a cathode and anode). The ion-exchange membrane divides (or separates) the cell or container into two, fluid-tight compartments, each containing one electrode. Chemical reactants are introduced into both compartments and either given, or stripped of, electric charge on contact with 20 the electrode in that compartment. Charged reactant species in one compartment may migrate due to the applied electrical field, or diffuse due to a concentration gradient, through the membrane/separator from one compartment to another. Some ionic species preferentially pass through the ion-exchange membrane while others are hindered. The net result is a flow of 25 ions from one cell compartment, through the ion-exchange membrane, to the second compartment, where they react with the ionic species generated there, and in so doing either release or accept an electric charge from the electrode.

In some cases the three elements (anode, cathode and electrolyte) are constructed as three separate units. In others, such as PEM fuel cells, they are 30 permanently bonded together to form a single unit often referred to as a membrane electrode assembly (MEA). The electrode may simply be used as an element to supply or receive electrical charge, or it may be combined with a catalyst to promote reaction between the various reactants or reactant ions at

its surface, in which case it may be referred to as an electrocatalytic element or a catalytic electrode.

A further important component in PEM fuel cells is the gas diffusion media. This is commonly a micro- or macro-porous carbon paper or cloth placed adjacent to the catalyst layer or electrode to provide uniform distribution of reactants across the entire electrode. In some cases the electrodes may be attached to the gas diffusion media and then hot-pressed to the membrane to form an MEA with gas diffusion media attached. The hydrophobic or hydrophilic nature of the gas diffusion media may also be used to facilitate water management in the fuel cell.

Many systems employing ion-exchange membranes employ reactants which need to be separated from one another and securely maintained within the electrolytic cells. Often the reactants are valuable and need to be fully utilized for economic and efficient cell operation. Thus, any leakage of reactants is undesirable. In some cases, reactants are potentially hazardous or explosive, rendering leakage of reactants or products undesirable for safety considerations.

It has long been recognized by developers of electrochemical devices that sealing requirements are an important practical consideration in cell design. Many advanced electrochemical cell designs have been developed, but unless they incorporate proper sealing, these designs cannot provide the necessary utility expected by end users.

Often in electrochemical cells, the ion-exchange membrane itself performs part of the sealing function. However, there is additional cost incurred using ion-exchange material for a sealing function (which does not require any ion transfer) because a larger membrane or separator area than necessary must be used. The membranes used are often thick -- 5 to 7 mils (125 - 180 microns). In addition, use of the membrane edge as a sealing element may require contact between the membrane and current collectors in an electrolytic device (such as a fuel cell). This may result in contamination of the membrane or degradation of the current collector plates because the membrane is corrosive. A membrane compressed between current collectors may also become dehydrated when not in contact with reactants or water vapor, changing the physical characteristics of the membrane. Furthermore, if an

edge of an ion-exchange membrane comes into contact with contaminants at the external surface of the cell, the contaminants may be absorbed and introduced into the cell, resulting in performance losses.

Advances in membrane technology allow use of thinner (less than 7 mils thick, which is the thickness of commercially available NAFION® 117 film, DuPont, Wilmington, DE) composite ion-exchange membranes in electrolytic systems. Such composite membranes include a porous base material impregnated with an ion-exchange resin as described in U.S. Patent No. 5,599,614. While these composite membranes are strong and dimensionally stable, and they provide decreased cell resistance and simplify water management in fuel cells, thinness may be problematic in current cells designed for thicker separators. Moreover, where high cell clamping pressures are employed, thin membranes may not have sufficient sealing capability. Therefore, one object of this invention is to allow use of such thinner membranes without concern regarding their sealing function.

In recent years substantial effort has been invested in PEM fuel cell research. One development has been the lowering of precious metal catalyst loadings. This is achieved by using very thin catalyst layers (or electrodes) applied to the membrane. Electrodes prepared in prior technologies, by applying catalyst to the gas diffusion media, either a carbon paper or cloth, produced poor catalyst utilization and hence required much higher catalyst loadings. Thin film catalyst technology has greatly reduced the cost of PEM fuel cells, making commercialization increasingly attractive. One preferred method for continuous roll type manufacture of MEAs with low catalyst loadings is to deposit catalyst layers on both sides and to the edges of the membrane. In this case, the catalyst layers extend beyond the required active electrode area (typically the portion of the electrode covered by the gas diffusion media) necessary in the cell.

Traditional low volume MEA production techniques produce discrete MEAs in which a border of polymer electrolyte extends beyond the active electrode area. Gaskets for these systems extend from the edges of the active electrode area to the edge of the polymer electrolyte membrane, or beyond. The catalyst area is covered with a carbon paper or cloth gas diffusion material.

In compression, the gasket provides a fluid tight seal around the gas diffusion material.

If current methods of fuel cell gasketing are used in continuous manufactured MEAs with thin membranes and catalyst layers extending to the membrane edges and hence under the sealing elements, there is potential for membrane failure. Depending upon the fuel cell design, MEA failures may be found at interfaces where the catalyst layer extends under the sealing gasket and where the gasket meets the gas diffusion media. Therefore, another purpose of this invention is to provide MEA sealing designs which eliminate the potential for failure, especially of thin membranes at this interface.

A purpose of this invention is to enable minimum use of expensive catalytic or electrode materials as a sealing element in both continuously manufactured and discrete MEAs. Recent fuel cell designs employ a combined membrane electrode assembly as central "drop-in" components between two bipolar plates. These assemblies employ expensive catalyst or electrode material such as platinum or exotic carbon fibers which should be limited to use in areas where such material is absolutely necessary. Any use of these catalyst materials in the sealing area would produce additional cost and wasted resources. Moreover, provisions are made for automated assembly involving sealing elements.

The purpose of the sealing component is also to limit the possibility of the current collector plates or bi-polar plates (in a non-planar cell) from contacting one another and shorting. Thus, this invention relates to a gasket that is an electrically insulating, as well as sealing, element useful in such service. It is also important for gasket material to introduce no contaminants into the cell.

SUMMARY OF THE INVENTION

This invention provides an apparatus for an electrochemical cell comprising a polymer electrolyte membrane having a central portion, a peripheral portion and an electrode disposed over at least the central portion of the polymer electrolyte membrane and over a portion of the peripheral portion of the polymer electrolyte membrane, a sub-gasket disposed over the

peripheral portion of the polymer electrolyte membrane such that the sub-gasket also extends over the portion of the electrode extending over the peripheral portion of the polymer electrolyte membrane, and a gasket disposed over at least a portion of the sub-gasket.

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The sub-gasket is typically less than 50 µm and is placed between the primary gasket and the MEA. The sub-gasket is sized such that the area of gas diffusion media in contact with the catalyst layer is reduced. Using a sub-gasket and reducing the area of the gas diffusion material in contact with the catalyst layer effectively moves the interface between the gas diffusion material and the gasket, inside the active area of the cell and eliminates or reduces edge failure because entry gas does not impinge directly onto the catalyst layer through a gap between the gasket and the gas diffusion layer. Thus, hot spots where significantly more reaction occurs, and which can degrade the membrane over time, can be eliminated.

Improved bonding with gaskets in the cell is achieved by impregnating a porous gasketing material to some thickness, with an ionomer, thermoplastic, adhesive or other resin which is compatible with, and able to bond to, the ionomer contained in the MEA. The resin-imbibed surface of the gasket is then contacted with the MEA either while the resin is wet, or when it is dry, typically with some combination of heat and pressure. The portion of the sealing material furthest from the interface of the sealing element and the MEA may be impregnated with a different elastomer, adhesive or other conformable polymer. Alternatively, the gasket can be a non-porous thermoplastic material melt-bonded to adjacent components, or a porous material bonded to adjacent elements with an adhesive.

The sub-gasket may be made from the same or different material as the gasket. Components may be sealed together by compression in the assembled cell or by a melt or pressure adhesive. The gasket and sub-gasket may be strips or a frame of porous polymeric materials such as expanded polytetrafluoroethylene (ePTFE) or porous polypropylene, or alternatively strips or a frame of non-porous or partially porous composite materials such as Kraton® butadiene/styrene copolymer or Viton® hexafluoropropylene/vinylidene fluoride in composite with ePTFE, or materials

- such as polyvinylidene fluoride, tetrafluoroethylene/hexafluoropropylene copolymer, THV (a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride), poly(vinyl fluoride), ethylene/tetrafluoroethylene copolymer, ethylenetrichlorofluoroethylene, or PTFE or other thermoplastics or elastomers.
- 5 The gasket and sub-gasket are attached to the periphery or some part of the periphery of the MEA. The purpose of the gasket and sub-gasket is to form a fluid tight seal between the MEA and the gas diffusion media and the walls of the electrochemical cell in which it is installed, to minimize the quantity of the more expensive ionomer composite and electrocatalytic materials that would
- 10 otherwise be used as a gasketing material, to prevent mechanical failure of the MEAs, and to provide electrical insulation between components of the electrochemical cell which must remain electrically isolated for proper operation of the cell. The complete assembly is known as a membrane electrode gasket assembly (MEGA). When a sub-gasket is used, the assembly is known as a
- 15 membrane electrode sub-gasket assembly (MESGA).

BRIEF DESCRIPTION OF DRAWINGS

- Fig. 1 is a perspective view of a MEGA according to an exemplary embodiment of the invention.
- 20 Fig. 2 is a perspective view of a MESGA according to an exemplary embodiment of the invention with a sub gasket.
- Fig. 3 is a perspective view of a MEGA according to an exemplary embodiment of the invention.
- 25 Fig. 4a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.
- Fig. 4b is a top view of the MEGA of Fig. 3a.
- Fig. 5a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.
- 30 Fig. 5b is a top view of the MEGA of Fig. 5a.
- Fig. 6a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.
- Fig. 6b is a top view of the MEGA of Fig. 6a.
- Fig. 7a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.

Fig. 7b is a top view of the MEGA of Fig. 7a.

Fig. 8a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.

Fig. 8b is a top view of the MEGA of Fig. 8a.

5 Fig. 9a is a cross-sectional side view of a MEGA according to an exemplary embodiment of the invention.

Fig. 9b is a top view of the MEGA of Fig. 9a.

Fig. 10a is a cross-sectional side view of an unassembled MEGA according to an exemplary embodiment of the invention.

10 Fig. 10b is a cross-sectional side view of an assembled MEGA according to an exemplary embodiment of the invention.

Fig. 10c is a top view of the MEGA of Fig. 10a.

Fig. 11 is a cross-sectional view of a MESGA according to an exemplary embodiment of the invention including a sub-gasket in which the 15 MEA extends to the edge of the cell.

Fig. 12 is a cross-sectional view of a MESGA according to an exemplary embodiment of the invention including a sub-gasket in which the MEA is clamped between the gaskets.

20 Fig. 13 is a cross-sectional view of a MESGA according to an exemplary embodiment of the invention including a sub-gasket in which the MEA is clamped between the gaskets, and a spacer frame is included.

DETAILED DESCRIPTION OF THE INVENTION

Shown in Figure 1 is a perspective view of a MEGA according to an 25 exemplary embodiment of this invention. A gasket (1) is disposed on the periphery of a discrete MEA. The MEA is made up of an electrode (3) bonded to the central area of each side of a membrane (2). Generally, membrane (2) of the invention is less than 2 mils (50 microns) thick.

The membrane (2) and the electrode (3) may be combined in various 30 ways. For example, membrane (2) with electrode (3) bonded to one side only is known as a half-MEA. Membrane (2) with electrodes (3) bonded to both sides is known as an MEA. MEAs and half-MEAs may be assembled from free-standing individual component pieces. Electrodes (3) may first be prepared as decals on sheets of a suitable carrier material and then transferred

and bonded to membrane (2). Alternatively, electrodes (3) may be applied directly to membrane (2) by painting or spraying, for example.

Figure 2 shows a perspective view of a MESGA according to an alternative embodiment of the invention incorporating both a gasket (1) and a 5 sub-gasket (4). Sub-gasket (4) is disposed on the periphery of a continuously manufactured MEA. Gasket (1) is then bonded to sub-gasket (4) such that an inside portion (4a) of sub-gasket (4) remains visible.

Gasket (1) or sub-gasket (4) may be attached to membrane (2) or to electrode (3), or to both, in any one of several ways. Figure 3 shows a 10 preferred embodiment for a MEGA according to this invention without sub-gasket (4) in which two membranes (2) (substantially non-porous composites of ePTFE and an ion-exchange polymer, such as is taught in U.S. Patent No. 5,547,551), are each coated on one side with an electrode (3). The two half-MEAs are then bonded together such that their uncoated sides are in contact, 15 with the exception of a narrow margin on two opposing and parallel edges 2(a) of the membranes' periphery. Strips of ePTFE gasket (1), coated with a solution of the same ion-exchange polymer used in membranes (2), are sandwiched between and bonded to the two membranes (2) along both these parallel edges 2(a). A portion of the ePTFE strips protrude beyond the edges 20 (2a) of the membranes to which they are bonded, and provide the requisite seal between the plates of the electrochemical cell. In this embodiment the seal is provided on two sides only, thereby allowing the elements to be made continuously.

The preferred MEGA of the present invention without sub-gasket (4) 25 has three basic components:

1. gasket (1) containing ion-exchange polymer which covers at least part of the periphery of the membrane or the MEA (the central ungasketed area of the assembly (covered by a gas diffusion medium in use) defines its active electrode area);
- 30 2. membrane (2) containing ion-exchange polymer which extends beyond the active area to provide an overlap with gasket (1) for effectively bonding gasket (1) to membrane (2) through contact between the ion-exchange resin of gasket (1) and of membrane (2); and

3. one or two electrodes (3) which completely cover one or both surfaces of the active area (optionally, the electrodes (3) may extend beyond the active area, although this would not represent optimum utilization of the expensive catalyst).

5 Ion-exchange membranes are well known. These are porous membranes that have an ionomer resin on the membrane and/or in the pores of the membrane. A preferred membrane is a porous fluoropolymer, such as stretched porous PTFE. The ionomer resin can be, among others, a fluorinated polymer that has recurring units of $-SO_3H$ or $=COOH$.

10 Electrode (3) is a dispersion of catalyst (or catalyst supported on an electronic conductor), fluorinated ionomer and a binder such as PTFE (in some electrodes, the ionomer may act as a binder).

When membranes (2) extend peripherally beyond electrode (3), the
15 MEA is called a discrete MEA. In this case, there is an area around the periphery of electrode (3) where gasket (1) or sub-gasket (4) overlaps membrane (2) and, optionally, a portion of electrode (3) in order that ionomer in sub-gasket (4) or gasket (1) mates with ionomer in the MEA to facilitate firm bonding of these components with one other. In another alternative and
20 preferred embodiment for rapid manufacture, the MEA may be a continuous tape, with at least membrane (2) of the tape protruding beyond electrode (3). The protruding portion of membrane (2) may then be covered and bonded to gasket (1) or sub-gasket (4).

Gasket (1) and sub-gasket (4) may be combined with membranes (2),
25 electrode (3), half-MEAs, and MEAs in many ways with respect to the shape of components and the manner in which these components are joined in the thickness dimension. Gasket (1) and sub-gasket (4) are typically shaped to cover either a part or the entire periphery of membrane (2) and the periphery of electrode (3).

30 It is possible to bond gasket (1) or sub-gasket (4) to one side of membrane (2) or of an MEA. Alternatively, membrane (2) or an MEA may be bonded between two or more gaskets (1) (or gasket (1) - plus sub-gasket (4)) as in Figures 1 and 2, or gasket (1) may be bonded between two membranes (2) or half MEA's as in Figure 3.

When sub-gasket (4) is used, it is positioned so that it covers part or all of the periphery of the MEA. For continuously produced MEAs, sub-gasket (4) is necessary to prevent possible failure in the MEA at the interface of the gas diffusion media and gasket (1). Sub-gasket (4) extends into the active cell area (that area of electrode (3) surrounded by gasket (1) and normally covered by a gas diffusion media) and hence under the gas diffusion media by some distance, such as several millimeters. Gasket (1) is positioned over sub-gasket (4), typically having a larger inner cut-out area than sub-gasket (4). Gasket (1) is typically thicker than sub-gasket (4). Gasket (1) typically frames the gas diffusion media.

In the exemplary embodiment of Figure 3, where gasket (1) only covers part of the periphery of the MEA, gasket (1) is bonded to two opposing edges of a continuous sheet of membrane (2) or of an MEA. In this case, the inner edges of gasket (1) (i.e., those bordering or overlapping the active area of the fuel cell), may optionally be beveled, milled, or rabbeted in order to facilitate gas tight joints with sealing members on the remaining two sides of the assembly. Generally, if less than four sides of the planar surface of membrane (2) are connected with one type of gasket (1), other sides of membrane (2) may use another gasket (or other sealing means) which may or may not be connected to the sides having gaskets (1) attached thereto.

These components may be assembled using discrete parts or, to facilitate continuous production line manufacture, could be assembled from continuous lengths of appropriately formed gasket material and membrane or MEA, then cut into individual pieces to form the final MEGA after bonding.

Gasket (1) or sub-gasket (4) may be made from chemically resistant materials that are sufficiently conformable to block the flow of fluids when used in an electrochemical cell. Elastomeric polymer materials and membranes, porous polymeric membranes, or in some cases porous polymeric membranes imbibed with some polymeric or elastomeric material may be used.

In a preferred embodiment, gasket (1) and sub-gasket (4) are each a porous PTFE membrane available from W. L. Gore & Associates, Newark, DE. This PTFE membrane may be partially or fully imbibed with a polymeric resin and subsequently connected (typically by application of heat and pressure) to the assembly at the periphery of membrane (2) and/or electrode (3). The

polymeric resin may alternatively be present as a coating on the surface of gasket (1). The polymeric resin preferred is an ion-exchange resin identical to or similar to the resin in membrane (2). Thus, bonding, mechanical compatibility, and chemical compatibility between gasket (1), membrane (2), and sometimes electrode (3), is promoted. Other polymeric resins may also be used. Examples of such materials include fluoropolymers, silicones, polyolefins, etc. In addition, an adhesive may also be used. The purpose of the polymeric resin is to fully occlude at least part of the structure to block fluid transport and form an adhesive bond between components; i.e., provide a seal.

Many porous or partially porous conformable media may be suitable as gasket (1) or sub-gasket (4) (which may be made of different materials). Specifically, polymeric structures made from PVDF, PE, PP, etc., may be used. The gasket material should ideally contribute to the reinforcement of the imbibed resin and also provide an interlocking structure around which the imbibed resin can form and promote bonding. Alternatively, a non-porous thermoplastic material can be used as the gasket material and melt-processed or coated with an adhesive to form a seal.

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EXAMPLES

Example 1 (See Figures 4a,b):

Two sheets of expanded polytetrafluoroethylene (ePTFE) five mils thick were cut to 10" x 10" using a steel rule die. One side of each sheet was brushed with a solution containing 4% by weight perfluorosulfonic acid (PFSA) 25 resin with a 950 equivalent weight, sold under the name Flemion by Asahi Glass, in a solvent mixture of 50% water and 50% ethanol. The solution did not penetrate the sheets, but merely coated their surfaces. The solution was allowed to dry on the sheets to form a dry ionomer coating (5). A 7" x 7" square was cut out of the center of each sheet using a steel rule die. An MEA 30 of a membrane (2) bonded to two electrodes (3) made by the teachings of U.S. patent 5,635,041 was assembled. Each electrode (3) was 7" x 7" and the two electrodes (3) were centered on membrane (2) which measured 8" x 8". The two sheets of coated ePTFE (gaskets (1)) were placed on the MEA such that the cut-away region of the ePTFE sheet framed the catalyzed region of the

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MEA and such that the coated side of the sheets were placed against the uncatalyzed membrane (2) around the peripheral portion of membrane (2) as shown. The assembly was heated to 140°C for three minutes in a press using 300 psi pressure. After this treatment, the ePTFE sheets adhered to 5 membrane (2) of the MEA.

Example 2 (See Figures 5a,b):

A sheet (6) of skived THV polymer eight mils thick was placed against an ePTFE membrane (7) 0.5 mils thick having an average pore size of 0.2 mils 10 (THV is a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride.) The two materials were heated in a press at 200°C and 200 psi for four minutes. This caused THV sheet (6) to bond to the ePTFE membrane (7). The exposed ePTFE side of the resulting structure was then brushed with a solution containing 9 wt% perfluorosulfonic acid resin in ethanol (Flemion 15 solution from Asahi Glass). The porous microstructure of the ePTFE membrane became substantially occluded with the PFSA resin, which also formed a layer (8) on ePTFE membrane (7). This composite sheet was trimmed to 10" x 10". A square 7" x 7" was cut from the center of the sheet. This sub-assembly formed gasket (1). An MEA similar to the one used in 20 Example 1, again including a membrane (2) and two electrodes (3), was placed against gasket (1) such that the catalyzed area lined up with the cut-away area of gasket (1) and such that the PFSA side of gasket (1) was placed against the uncatalyzed membrane of the MEA. The assembly was heated to 140°C for three minutes in a press using 300 psi pressure. After this treatment, gasket 25 (1) adhered to the ionomer composite membrane.

Example 3 (see Figures 6a,b):

Two sheets of expanded polytetrafluoroethylene (ePTFE) five mils thick were cut to 10" x 10" using a steel rule die. One side of each sheet was 30 brushed with a solution containing 4% by weight perfluorosulfonic acid resin (950 EW) (Flemion, from Asahi Glass) in a solvent mixture of 50% water and 50% ethanol. The solution did not penetrate the sheets, but merely coated the surface. The solution was allowed to dry on the sheets to form a dry ionomer coating (5). A 7" x 7" square was cut out of the center of each sheet using a

steel rule die. Each cut and coated ePTFE sheet forms a gasket (1). A continuous roll of MEA was prepared, in which membrane (2) was a roll of 30 micron PFSA/ePTFE composite membrane made by the teaching of U.S. Patent No. 5,547,551 and was continuously coated with a catalyst ink, completely covering both sides of membrane (2) to form two continuous electrodes (3), according to the teaching of U.S. Patent No. 5,635,041. The MEA was eight inches wide and made in a continuous length. A square 8" x 8" MEA was cut from this roll. The MEA was placed on top of one ePTFE sheet centered over the 7" x 7" cut-out region such that the PFSA coated side of the ePTFE sheet faced the MEA. The other ePTFE sheet was placed on top of the MEA, also centered, such that the PFSA coated side faced the MEA. The assembly was hot pressed at 140°C for three minutes at 200 psi pressure. The result was an MEA with an integral bonded gasket assembly in which the MEA portion was made by a continuous process.

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Example 4 (see Figures 7a,b):

A roll of PFSA/ePTFE composite membrane was produced which was 8" wide. This formed membrane (2). A strip of catalyst ink 7" wide was applied to the center of the membrane roll on both sides such that 0.5" of membrane on either side remained uncatalyzed. The catalyzed regions on each side of membrane (2) form electrodes (3), and together these components form a continuous roll of MEA. A roll of expanded PTFE sheet five mils thick and 1.5 inches wide was provided as material for the gasket (1). This roll was coated on one side with PFSA solution (Flemion solution from Asahi Glass) and was allowed to dry to form an ionomer coating (5) as in the previous examples. The coated side was laminated to the edge of the MEA roll such that the catalyzed region lined up with the edge of the ePTFE sheet and the ePTFE sheet did not overlap the catalyzed region. Another length of ePTFE was laminated to the other edge of the membrane in the same manner. Similarly, the ePTFE sheet was laminated to the opposite side of these edges. The result was a continuous length of membrane electrode gasket assembly in which gaskets (1) exists on two edges of the assembly only.

Example 5 (see Figures 8a,b):

A piece of porous polypropylene 10" x 10" was impregnated with PFSA solution (Nafion from duPont) via the teaching of U.S. Patent No. 5,547,551 to form membrane (2). Two pieces of solution cast polyurethane sheet, five mils thick, were cut to 10" x 10" and a region 7" x 7" was cut out of the center of each sheet. These sheets were laminated to the composite membrane by heating in a press at 120°C for one minute under 200 psi pressure to form gasket (1). The orientation of the sheets was such that the openings of the two pieces of polyurethane lined up on either side of the membrane. The assembly was now placed on a table and a catalyst ink mixture was screen printed onto the ungasketed region in the center to form electrode (3). The same procedure was repeated on the reverse side.

Example 6 (see Figures 9a,b):

A roll of ePTFE/PFSA composite membrane (2) 10" wide was prepared according to the teaching of U.S. Patent No. 5,547,551. An electrode (3) was formed by applying catalyst to both sides of membrane (2) in a strip 7" wide centered over membrane (2) to form a roll of MEA material. A roll of ePTFE ten mils thick and 10" wide was laminated to a roll of double-sided pressure sensitive adhesive using pressure but no heat. The roll was then run through a rotary die in which 7" x 7" squares were cut from the center of the roll at regular intervals in which each square was six inches from the next square. The MEA roll was continuously laminated to the ePTFE roll such that the adhesive bonded the ePTFE material to the MEA to form gasket (1). The procedure was repeated on the other side of the MEA roll such that the 7" x 7" openings on the first side lined up with the openings on the other side. The result was a continuous roll of gasketed MEA from which individual membrane electrode gasket assemblies could be cut (10" x 10" outer dimensions).

Example 7 (see Figures 10a,b,c):

Two rolls of 20 micron ePTFE/PFSA composite membrane (2) 8" wide were prepared according to the teaching of U.S. Patent No. 5,547,551. One side of each membrane was coated with a catalyst ink all the way to the edge to form an electrode element 8" wide according to the teaching of U.S. Patent No. 5,635,041. Two rolls of ePTFE membrane 1.5" wide and three mils thick

were prepared as gaskets (1). The MEA rolls were placed on either side of the two ePTFE rolls as shown in figure 10a below. The assembly was laminated at 150°C in a hot roll. The result was a membrane electrode gasket assembly containing only one layer of gasket at each edge as shown in figures 10b and

5 c.

Example 8 (see Figure 11):

Two sheets of expanded polytetrafluoroethylene (ePTFE) two mils thick were cut to 10" x 10" using a steel rule die. Both sides of each sheet were
10 brushed with a solution containing 4% by weight perfluorosulfonic acid (PFSA) resin with a 950 equivalent weight, sold under the name Flemion by Asahi Glass, in a solvent mixture of 50% water and 50% ethanol. The solution did not penetrate the sheets, but merely coated their surfaces. The solution was allowed to dry on the sheets to form a dry ionomer coating. A 6.875" x 6.875"
15 square was cut out of the center of each sheet using a steel rule die. A 10" x 10" piece of MEA was cut from a continuously manufactured roll of 10" wide membrane with catalyst layer electrode making a 7" wide stripe down the center of the roll. Therefore 1.5 " of membrane was exposed on two sides of the catalyst layer, but the catalyst layers extended to the edges of the other two
20 sides. The two sheets of coated ePTFE (sub-gaskets (4)) were placed on the MEA such that a square of 6.875 x 6.875 of electrode area was exposed. A piece of 10" x 10" silicon rubber 10 mils thick was cut out with a 7" x 7" square center removed. The silicon rubber gasket (1) was placed on top of the ePTFE/PFSA composite such that 6.875" x 6.875" of electrode area and 0.125"
25 border of ePTFE/PFSA composite (sub-gasket (4)) were exposed around the edges of the electrode (3). The assembly was heated to 140°C for three minutes in a press using 300 psi pressure. After this treatment the ePTFE sheets adhered to the MEA and the silicon rubber gasket (1). A cross section of the assembly with the MEA, ePTFE/PFSA sub-gasket and silicon rubber
30 gasket or sealing component are shown in Figure 11.

Example 9 (see Figure 12):

Two sheets of skived FEP 1 mil thick were cut to 10" x 10" using a steel rule die. A 6.875" x 6.875" square was cut out of the center of each sheet

using a steel rule die. The top and bottom of the FEP frame was painted with perfluorinated adhesive. A 8" x 8" piece of MEA was cut from a continuously manufactured tape of 8" wide membrane with catalyst layer electrode making a 7" wide stripe down the center of the roll. Therefore, 0.5" of membrane was exposed on two sides of the MEA, and catalyst layer extended to the edges of the other two sides. The two FEP adhesive coated sheets forming sub-gaskets (4) were placed on opposite sides of the MEA such that a square of 6.875" x 6.875" of electrode area was exposed. A piece of 10"x10" silicon rubber 10 mils thick was cut out with a 7 x 7" center removed. Silicon rubber gasket (1) was placed on top of the FEP such that 6.875" x 6.875" of electrode area and 0.125 " FEP composite were exposed. The assembly was heated to 140°C for three minutes in a press using 300 psi pressure. After this treatment the FEP sheets adhered to themselves at the assembly periphery, to the MEA, and to the silicon rubber. The assembly with the MEA, FEP sub-gasket, and silicon rubber gasket or sealing component are shown in Figure 12.

Example 10 (see Figure 13):

Two sheets of skived THV 1 mil thick were cut to 10" x 10" using a steel rule die. A 6.875" x 6.875" square was cut out of the center of each sheet using a steel rule die. A spacer frame (11) of FEP 0.002" (2 mils) thick, with outside 10" x 10" and internal cut out 8" x 8" was prepared. A 8" x 8" piece of MEA (also 0.002" (2 mils) thick) was cut from a continuously manufactured roll of 8" wide membrane with catalyst layer electrode making a 7" wide stripe down the center of the tape. Therefore, 0.5" of membrane was exposed on two sides of the MEA and electrode (3) extended to the edges of the other two sides. FEP spacer frame (11) was disposed around the MEA. The two THV sheets forming sub-gaskets (4) were placed on opposite sides of the MEA and FEP spacer frame (11) such that a square of 6.875" x 6.875" of electrode area was exposed. Further a piece of 10 x 10 " silicon rubber gasket 10 mils thick was cut out with a 7" x 7" center removed. The silicon rubber frame was gasket (1) and was placed on top of the THV sub-gasket (4) such that 6.875" x 6.875" of electrode area and 0.125 " THV composite were exposed. The assembly was heated to 140°C for three minutes in a press using 300 psi pressure. After this treatment, the sub-gaskets (4) adhered to the FEP frame, the MEA and the

silicon rubber. The assembly with the MEA , FEP, THV sub-gasket, and silicon rubber gasket or sealing component are shown in Figure 13.

The preceding description and examples are meant to illustrate the invention and not limit it. Those skilled in the art may develop alternative 5 embodiments of this invention, which are contemplated to be covered hereby. The invention should be interpreted in accordance with the full scope of the appended claims, including equivalents.

What is claimed is:

1. An apparatus for an electrochemical cell comprising:
 - a polymer electrolyte membrane having a central portion and a peripheral portion;
 - 5 an electrode disposed over said central portion of said polymer electrolyte membrane and over a portion of said peripheral portion of said polymer electrolyte membrane;
 - a sub-gasket disposed over said peripheral portion of said polymer electrolyte membrane such that said sub-gasket also extends over the portion of the electrode extending over the peripheral portion of the polymer electrolyte membrane; and
 - 10 a gasket disposed over at least a portion of said sub-gasket.
- 15 2. An apparatus according to claim 1, wherein said polymer electrolyte membrane is formed of a support structure impregnated with ion-exchange material.
- 20 3. An apparatus according to claim 2, wherein said support structure is expanded polytetrafluoroethylene and said ion-exchange material is an ion-exchange polymer.
- 25 4. An apparatus according to claim 1, wherein said electrode is an electrocatalytic element comprising a conductive material, a catalyst, and a binder.
5. An apparatus according to claim 4, wherein said conductive material is carbon, said catalyst is platinum, and said binder is ion-exchange material.
- 30 6. An apparatus according to claim 4 further comprising PTFE or ePTFE.
7. An apparatus according to claim 1, wherein said sub-gasket comprises polytetrafluoroethylene or expanded polytetrafluoroethylene.

8. An apparatus according to claim 1, wherein said sub-gasket comprises a thermoplastic polymer.
9. An apparatus according to claim 1, wherein said gasket
5 comprises polytetrafluoroethylene or expanded polytetrafluoroethylene.
10. An apparatus according to claim 1, wherein said gasket comprises a thermoplastic polymer.
- 10 11. An apparatus according to claim 1, wherein said gasket and sub-gasket are comprised of the same material.
12. An apparatus according to claim 1, wherein said sub-gasket is formed of a support structure impregnated with an ion-exchange material.
15
13. An apparatus according to claim 1, wherein said gasket is formed of a support structure impregnated with an ion-exchange material.
14. An apparatus according to claim 2, wherein said sub-gasket is formed
20 of a support structure impregnated with an ion-exchange material and wherein said ion-exchange material in said polymer electrolyte membrane is the same as said ion-exchange material in said sub-gasket.
15. An apparatus according to claim 14, wherein said gasket is formed of a support structure impregnated with an ion-exchange material and wherein said ion-exchange material in said polymer electrolyte membrane is the same as
25 said ion-exchange material in both said sub-gasket and said gasket.
16. An apparatus according to claim 15, wherein said electrode comprises
30 an ion-exchange material and wherein said ion-exchange material in said polymer electrolyte membrane is the same as said ion-exchange material in said sub-gasket, said gasket, and said electrode.

20

17. An apparatus according to claim 1, further comprising a spacer frame disposed around an outer perimeter of said polymer exchange membrane.

18. An apparatus for an electrochemical cell comprising:

5 a polymer electrolyte membrane having two sides, each with a central portion and a peripheral portion;

an electrode disposed over said central portion of each of said two sides of said polymer electrolyte membrane and over a portion of said peripheral portion of each of said two sides of said polymer electrolyte 10 membrane;

a sub-gasket disposed over said peripheral portion of each of said two sides of said polymer electrolyte membrane such that said sub-gasket also extends over the portion of the electrode extending over the peripheral portion of the polymer electrolyte membrane; and

15 a gasket disposed over at least a portion of each said sub-gasket.

19. An apparatus according to claim 18, wherein said gas diffusion media is disposed over each said electrode.

20. A fuel cell comprising a plurality of the apparaata defined in claim 19.

21. In a membrane electrode assembly having a polymer electrolyte membrane, an electrode disposed over said polymer electrolyte membrane, and a gasket disposed over part of either or both of said polymer electrolyte 25 membrane and said electrode, the improvement comprising a sub-gasket disposed between said gasket and either or both of said polymer electrolyte membrane and said electrode.

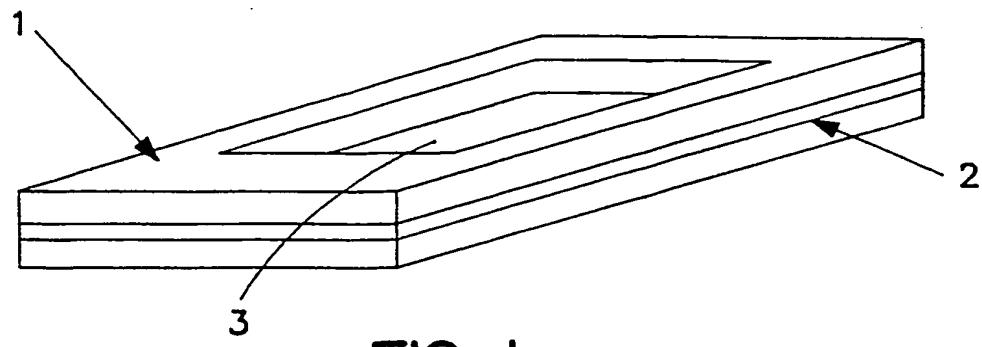


FIG. 1

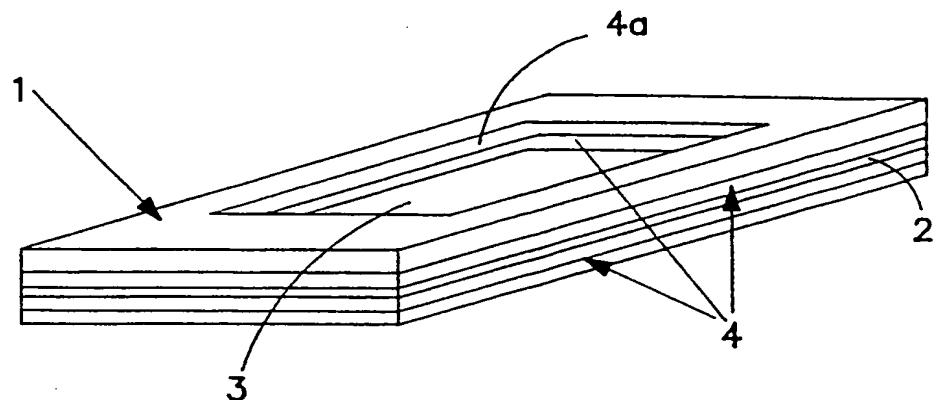


FIG. 2

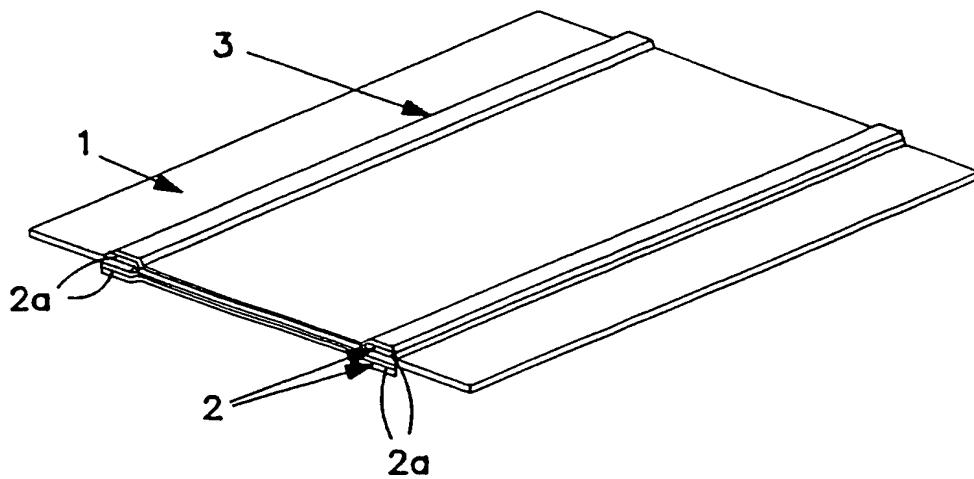


FIG. 3

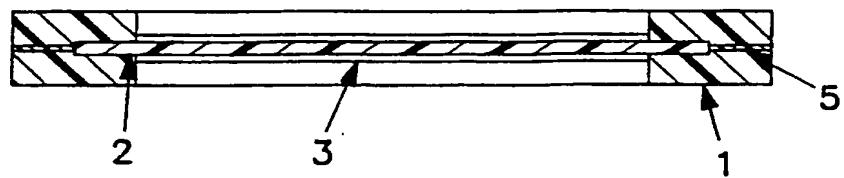


FIG. 4a

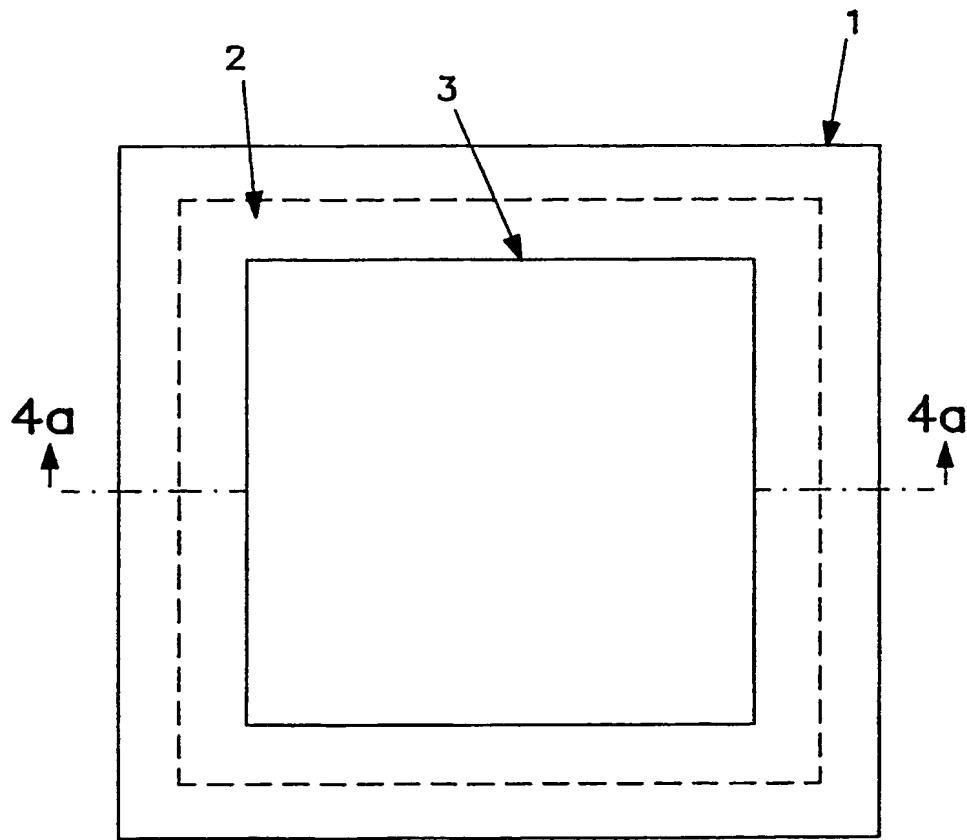


FIG. 4b

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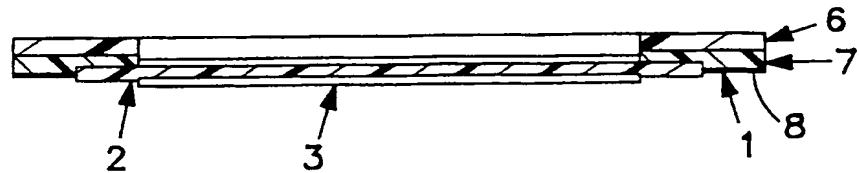


FIG. 5a

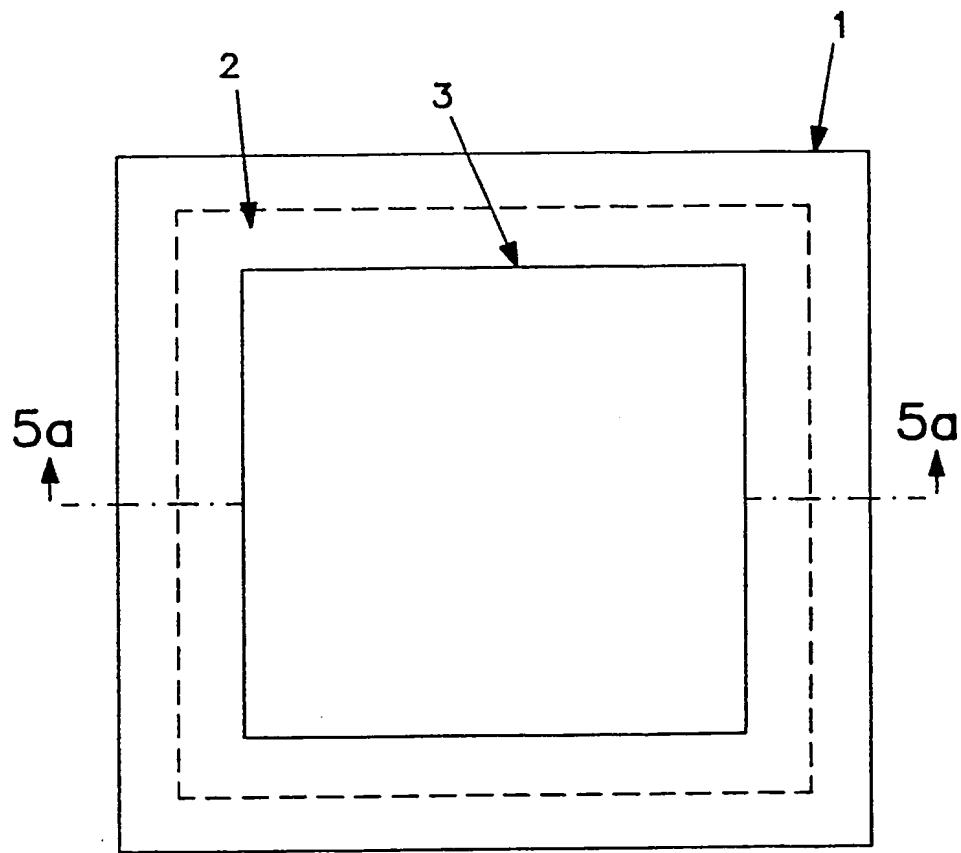


FIG. 5b

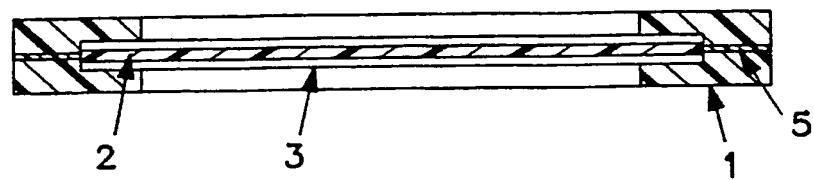


FIG. 6a

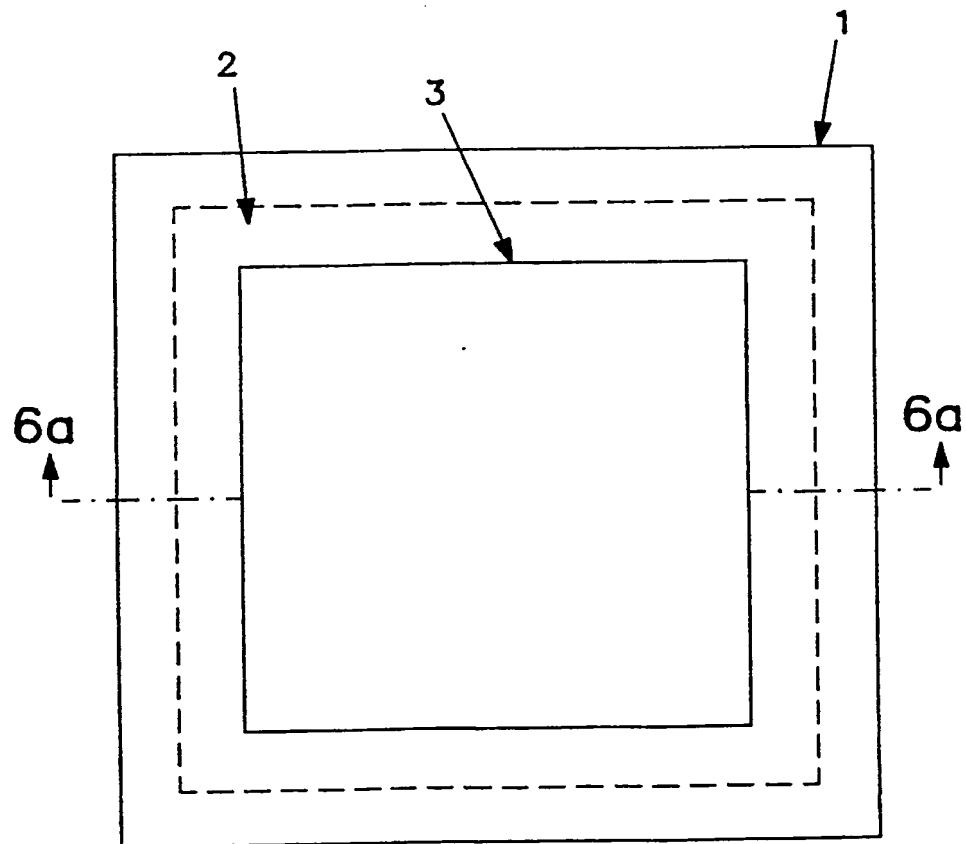


FIG. 6b

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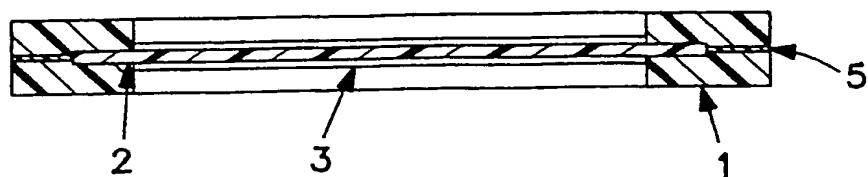


FIG. 7a

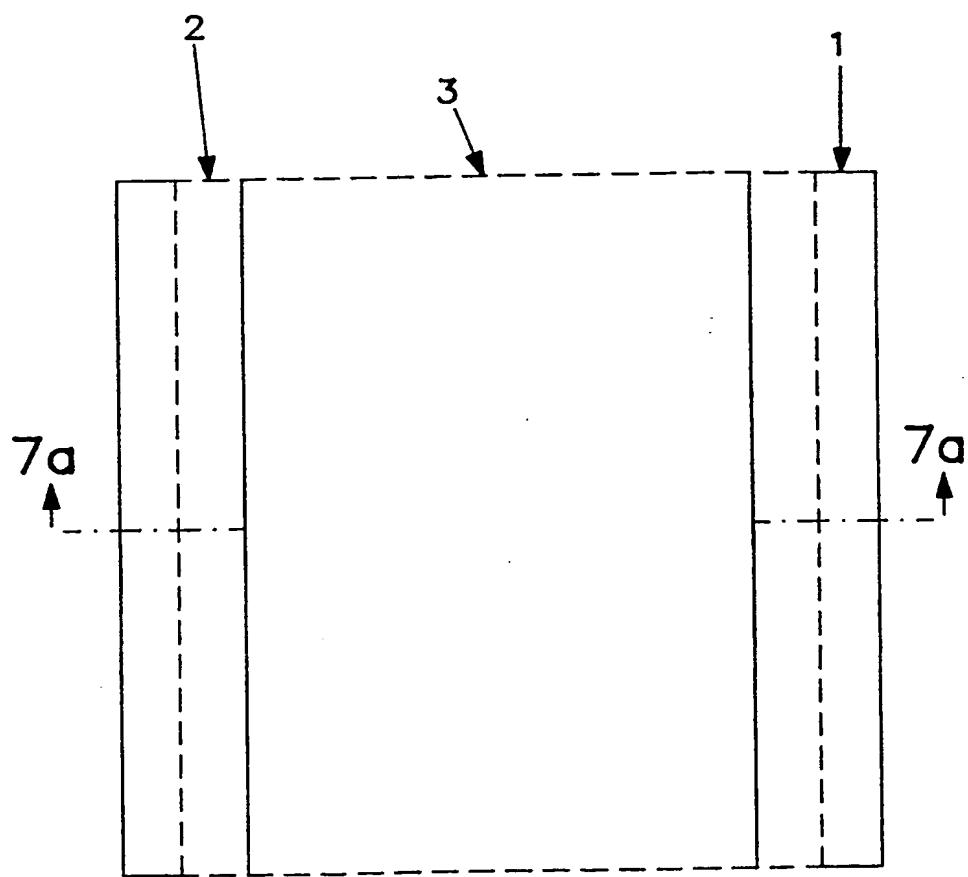


FIG. 7b

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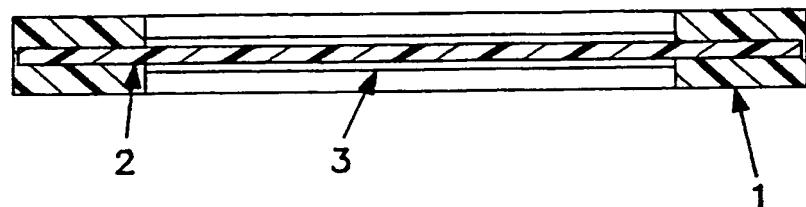


FIG. 8a

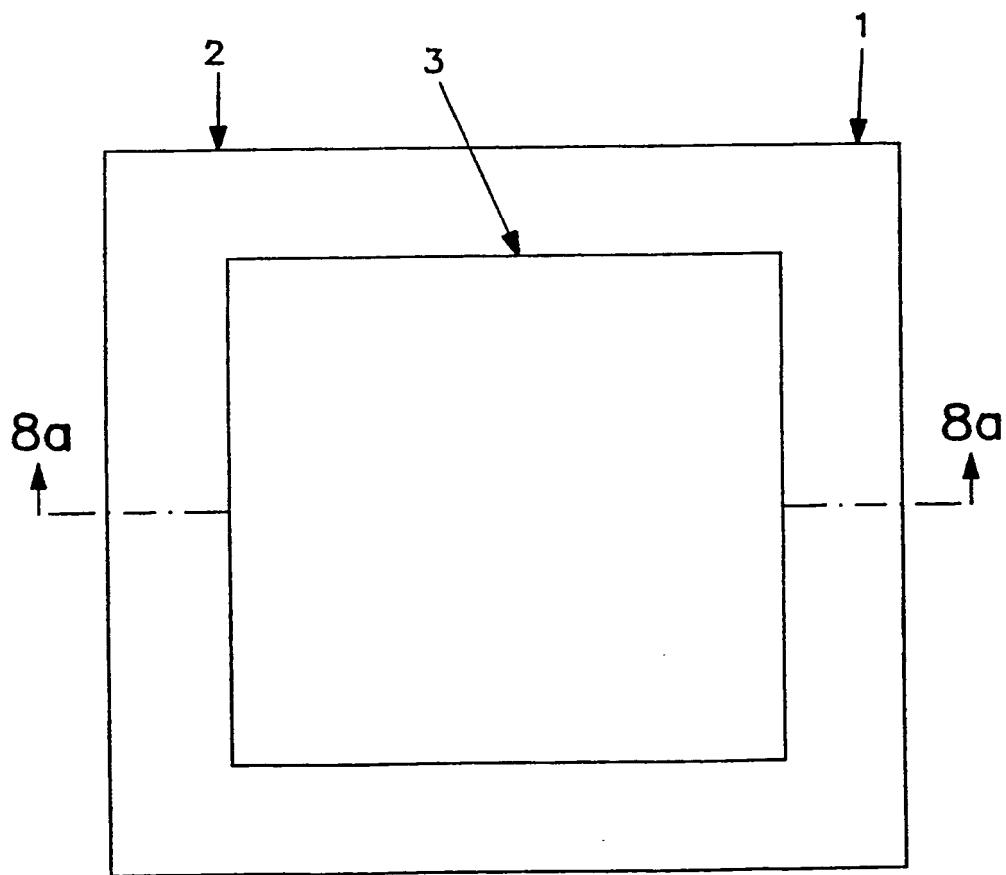


FIG. 8b

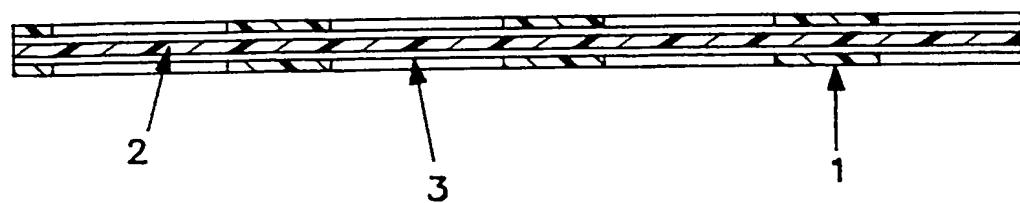


FIG. 9a

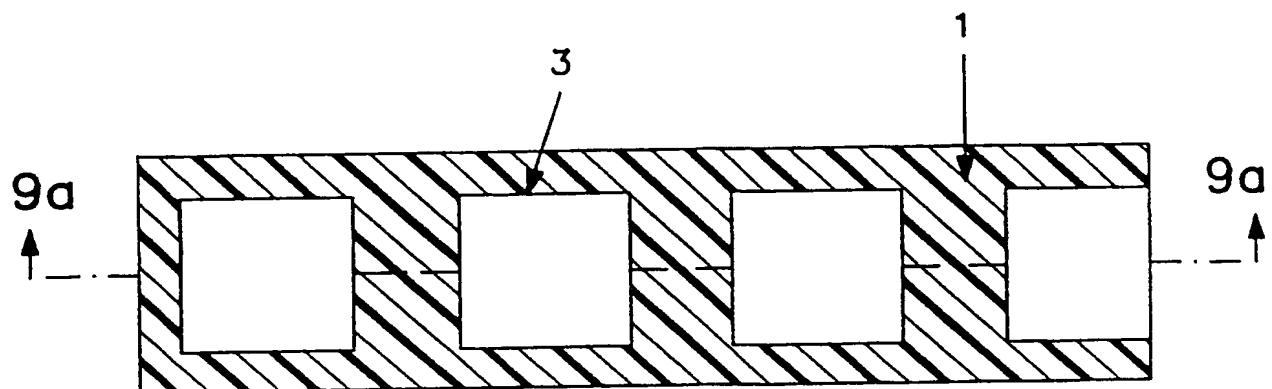


FIG. 9b

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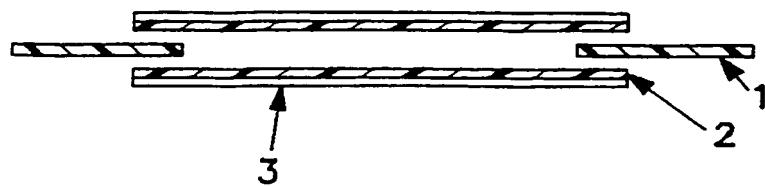


FIG. 10a

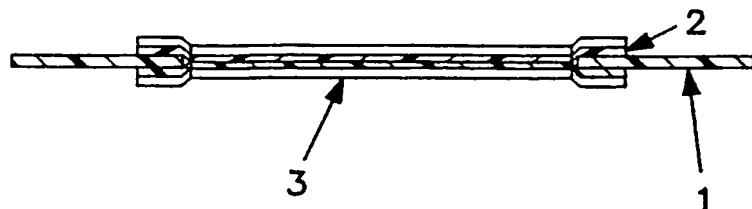


FIG. 10b

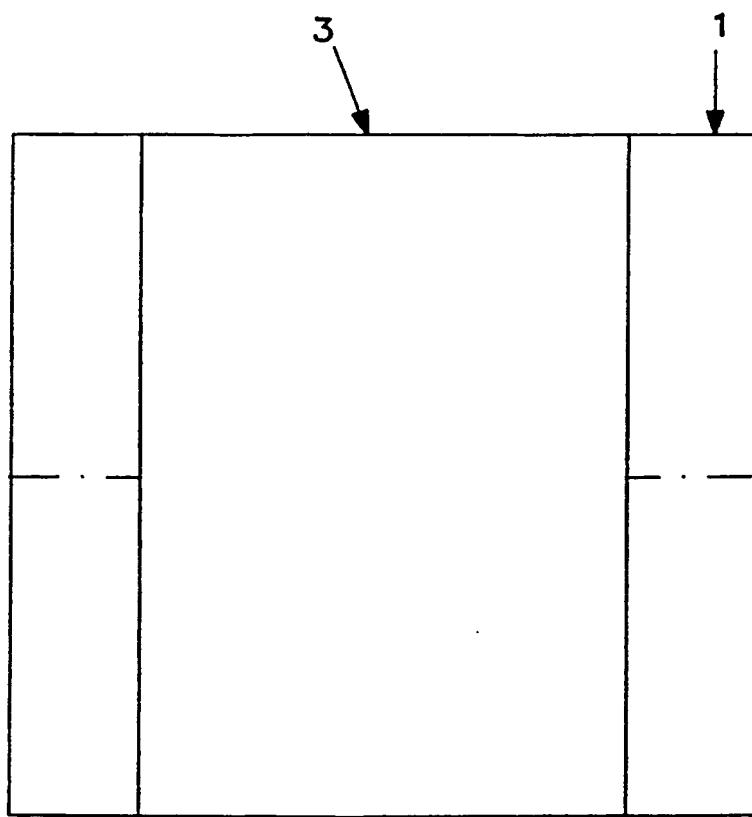


FIG. 10c

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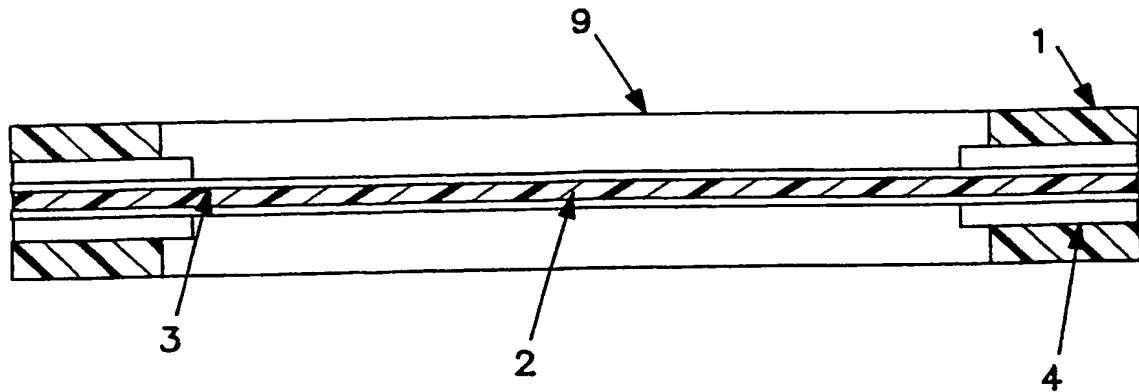


FIG. 11

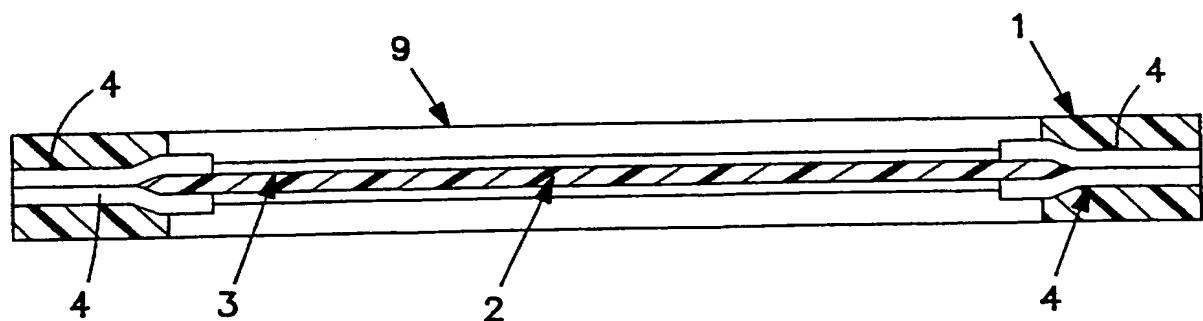


FIG. 12

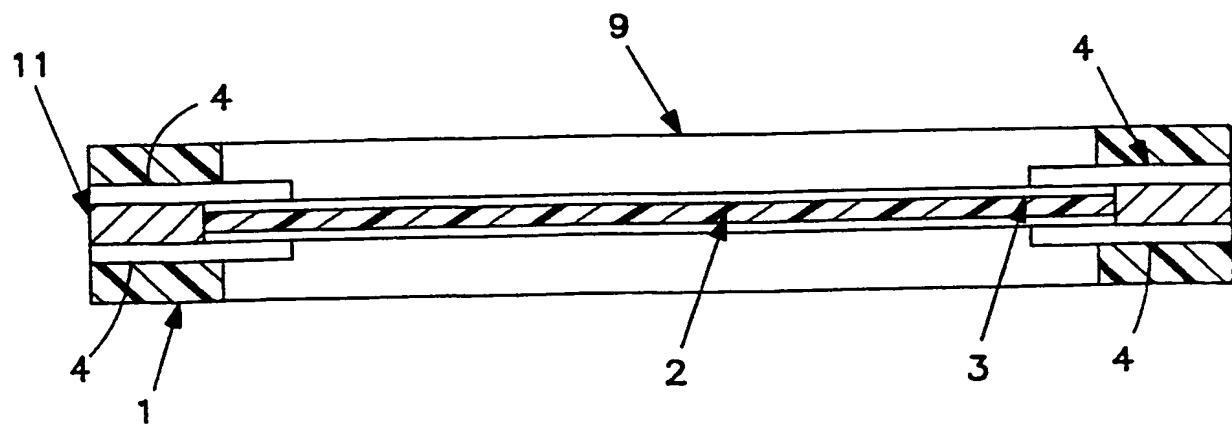


FIG. 13

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/18051

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01MB/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 187 025 A (KELLAND JAMES W ET AL) 16 February 1993 (1993-02-16) the whole document ----	1-6,18, 21
A	WO 98 33225 A (MAGNET MOTOR GMBH ;KOSCHANY ARTHUR (DE); SCHWESINGER THOMAS (DE)) 30 July 1998 (1998-07-30) claims 1-37 ----	1-21
A	EP 0 774 794 A (DAIMLER BENZ AG) 21 May 1997 (1997-05-21) claims 1-5 -----	1-21

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

9 November 1999

Date of mailing of the international search report

16/11/1999

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Battistig, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/18051

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5187025	A 16-02-1993	NONE		
WO 9833225	A 30-07-1998	DE 19703214 C AU 6617298 A		05-11-1998 18-08-1998
EP 0774794	A 21-05-1997	DE 19542475 A US 5928807 A		22-05-1997 27-07-1999

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